

11/17/00  
JC715 U.S. PTO

**UTILITY  
PATENT APPLICATION  
TRANSMITTAL**

(Only for new nonprovisional applications under 37 CFR 1.53(b))

Attorney Docket No. 2000-1578A

Total Pages :

First Named Inventor or Application Identifier

Yoichi MORI et al.

Express Mail Label No.:

**APPLICATION ELEMENTS**

See MPEP chapter 600 concerning utility patent application contents.

ADDRESS TO: Assistant Commissioner for Patents  
Box Patent Application  
Washington, D.C. 20231

1. ☒ Fee Transmittal Form  
(Submit an original, and a duplicate for fee processing)

6. Microfiche Computer Program (Appendix)

2. ☒ Specification [Total Pages - 13]  
(preferred arrangement set forth below)  
- Descriptive title of the Invention  
- Cross References to Related Applications  
- Statement Regarding Fed sponsored R & D

7. ☐ Nucleotide and/or Amino Acid Sequence Submission  
(if applicable, all necessary)

- a. ☐ Computer Readable Copy  
b. ☐ Paper Copy (identical to computer copy)  
c. ☐ Statement verifying identity of above copies

- Reference to Microfiche Appendix  
- Background of the Invention  
- Brief Summary of the Invention  
- Brief Description of the Drawings (if filed)  
- Detailed Description  
- Claim(s)  
- Abstract of the Disclosure

**ACCOMPANYING APPLICATION PARTS**

3. ☒ Drawing(s) (35 USC 113) [Total Sheets - 1]

8. ☒ Assignment Papers (cover sheet & document(s))

4. ☒ Oath or Declaration [Total Pages - 3]

9. ☐ 37 CFR 3.73(b) Statement ☐ Power of Attorney  
(when there is an assignee)

a.1. ☒ Newly executed (original or copy)

10. ☐ English Translation Document (if applicable)

a.2. ☐ Unexecuted

11. ☐ Information Disclosure Statement (IDS)/PTO-1449  
☐ Copies of IDS Citations

b. ☐ Copy from a prior application (37 CFR 1.63(d))  
(for continuation/divisional with Box 17 completed)  
[Note Box 5 below]

12. ☒ Preliminary Amendment

i. ☐ DELETION OF INVENTOR(S)

13. ☒ Return Receipt Postcard (MPEP 503)  
(Should be specifically itemized)

Signed statement attached deleting inventor(s)  
named in the prior application, see 37 CFR  
1.63(d)(2) and 1.33(b).

14. ☐ Small Entity Statement(s)

☐ Statement filed in prior application, Status still proper and desired

5. ☐ Incorporation By Reference  
(usable if Box 4b is checked)

15. ☒ Certified Copy of Priority Document(s)  
(if foreign priority is claimed)

The entire disclosure of the prior application, from which  
a copy of the oath or declaration is supplied under Box  
4b, is considered as being part of the disclosure of the  
accompanying application and is hereby incorporated by  
reference therein.

16. ☐ Other

THE COMMISSIONER IS AUTHORIZED  
TO CHARGE ANY DEFICIENCY IN THE  
FEE FOR THIS PAPER TO DEPOSIT  
ACCOUNT NO. 23-0975.

17. If a CONTINUING APPLICATION, check appropriate box and supply the requisite information:  
☐ Continuation ☐ Divisional ☐ Continuation-in-part (CIP) of prior Application No.

**18. CORRESPONDENCE ADDRESS**

WENDEROTH, LIND & PONACK, L.L.P.  
2033 "K" Street, N.W.  
Suite 800  
Washington, D.C. 20006  
Phone:(202) 721-8200  
Fax:(202) 721-8250

November 17, 2000

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re application of :

Yoichi MORI et al. :

Serial No. NEW :

Attn: APPLICATION BRANCH

Filed November 17, 2000 :

Attorney Docket No. 2000-1578A

METHOD AND APPARATUS FOR  
TREATING A WASTE GAS CONTAINING  
FLUORINE-CONTAINING COMPOUNDS :

THE COMMISSIONER IS AUTHORIZED  
TO CHARGE ANY DEFICIENCY IN THE  
FEE FOR THIS PAPER TO DEPOSIT  
ACCOUNT NO. 23-0975.

PATENT OFFICE FEE TRANSMITTAL FORM

Assistant Commissioner for Patents  
Washington, DC 20231

Sir:

Attached hereto is a check in the amount of \$750.00 to cover Patent Office fees relating to filing the following attached papers:

New application ..... \$710.00

Assignment for Recordal ..... \$ 40.00

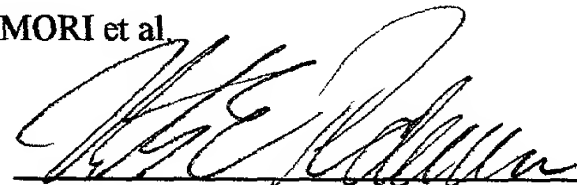
A duplicate copy of this paper is being submitted for use in the Accounting Division, Office of Finance.

*The Commissioner is authorized to charge any deficiency or to credit any overpayment associated with this communication to Deposit Account No. 23-0975, with the EXCEPTION of deficiencies in fees for multiple dependent claims in new applications.*

Respectfully submitted,

Yoichi MORI et al.

By:



Nils E. Pedersen  
Registration No. 33,145  
Attorney for Applicants

NEP/pth  
WENDEROTH, LIND & PONACK, L.L.P.  
2033 K St., N.W., Suite 800  
Washington, D.C. 20006  
Telephone (202) 721-8200  
November 17, 2000

[Check No. 40799 ]

2000-1578A

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re application of :  
Yoichi MORI et al. :  
Serial No. NEW : **Attn: Application Branch**  
Filed November 17, 2000 : **Attorney Docket No. 2000-1578A**

METHOD AND APPARATUS FOR  
TREATING A WASTE GAS CONTAINING  
FLUORINE-CONTAINING COMPOUNDS :

THE COMMISSIONER IS AUTHORIZED  
TO CHARGE ANY DEFICIENCY IN THE  
FEE FOR THIS FARMER TO DEPOSIT  
ACCOUNT NO. 23-0975.

**PRELIMINARY AMENDMENT**

Assistant Commissioner for Patents  
Washington, DC 20231

Sir:

Prior to examination of the instant application, please enter and consider the following amendments and remarks as follows:

**In The Claims:**

**Kindly amend claim 7 as follows:**

Claim 7. line 1, delete "or 6".

**Kindly add the following new claim 8:**

-- 8. The apparatus according to claim 6, which has not only an air ejector capable of adjusting the pressure in the apparatus through which the waste gas passes but also an FT-IR analyzer for controlling the emission density of the treated gas.--

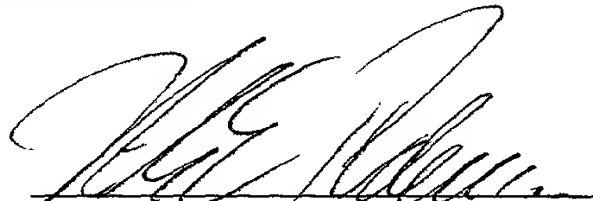
**REMARKS**

The present Preliminary Amendment is submitted to delete the multiple dependency of claim 8, thereby placing such claim in condition for examination and reducing the required PTO filing fee.

Respectfully submitted,

Yoichi MORI et al.

By:



Nils E. Pedersen

Registration No. 33,145

Attorney for Applicants

NEP/pth  
Washington, D.C.  
Telephone (202) 721-8200  
Facsimile (202) 721-8250  
November 17, 2000

METHOD AND APPARATUS FOR TREATING A WASTE GAS  
CONTAINING FLUORINE-CONTAINING COMPOUNDS

BACKGROUND OF THE INVENTION

This invention relates to the treatment of a waste  
5 gas containing fluorine-containing compounds. More  
particularly, it relates to a method and an apparatus for  
efficient treatment of emissions from semiconductor  
fabrication plants, particularly from the steps of dry  
cleaning the inner surface of a fabrication apparatus  
10 and etching various kinds of deposited films with  
perfluorocarbons (PFCs) and halogenated hydrocarbons such  
as  $C_2F_6$ ,  $C_3F_8$ ,  $CHF_3$ ,  $SF_6$  and  $NF_3$ , said waste gases containing  
not only PFCs but also oxidizing gases such as  $F_2$ ,  $Cl_2$  and  
 $Br_2$ , acidic gases such as  $HF$ ,  $HCl$ ,  $HBr$ ,  $SiF_4$ ,  $SiCl_4$ ,  $SiBr_4$   
15 and  $COF_2$ , as well as  $CO$ .

Semiconductor fabrication plants use many kinds of  
harmful gases that can potentially pollute the environment.  
PFCs contained in waste gases that typically result from  
the etching and CVD steps are suspected of causing global  
20 warning and it is urgently needed to establish an effective  
system for their removal.

Various breaking and recovery techniques have  
heretofore been proposed for PFC removal. Catalytic  
thermal decomposition is one of the breaking techniques and  
25 uses versatile compounds such as Pt catalyst, zeolite-base  
catalysts, activated charcoal, activated alumina, alkali  
metals, alkaline earth metals and metal oxides. However,  
none of these catalytic compounds have proved completely  
satisfactory.

30 The waste gases discharged from the semiconductor  
fabrication process contain not only PFCs but also  
oxidizing gases such as  $F_2$ ,  $Cl_2$  and  $Br_2$ , acidic gases such  
as  $HF$ ,  $HCl$ ,  $HBr$ ,  $SiF_4$ ,  $SiCl_4$ ,  $SiBr_4$  and  $COF_2$ , as well as  $CO$ ;  
however, no method has yet been established that can  
35 realize a thorough and effective treatment of these harmful  
gases.

If one wants to treat oxidizing gases such as  $F_2$ ,  $Cl_2$   
and  $Br_2$  by a wet method, thorough treatment cannot be

achieved by the sole use of water. If alkali agents or reducing agents are also used, not only process control but also the treatment apparatus becomes complicated and, in addition, the cost of treatment increases.

5 To remove CO, it has to be decomposed with oxidizers such as those based on Cu or Mn. As for PFCs, it has been proposed to use alumina as an agent for removing them (Japanese Patent Public Disclosure No. 286434/1998) and this method is characterized by contacting C<sub>2</sub>F<sub>6</sub> with  
10 molecular oxygen. However, the lifetime of alumina is very short and the throughput or the amount of C<sub>2</sub>F<sub>6</sub> that can be treated for 100% decomposition is only 4.8 L/L; what is more, no effective way has been proposed to deal with CO that occurs as a by-product of C<sub>2</sub>F<sub>6</sub> decomposition, still  
15 less for the oxidizing gases and acidic gases that occur concomitantly with PFCs.

#### SUMMARY OF THE INVENTION

The present invention has been accomplished under these circumstances and has as an object providing a method  
20 for treating waste gases containing fluorine-containing compounds which achieves high percent decomposition of PFCs, which proves effective for a prolonged time and which simultaneously realizes effective removal of oxidizing gases, acidic gases and CO that are contained in the waste  
25 gases.

Another object of the invention is to provide an apparatus for implementing this method.

The first object of the invention can be attained by a method for treatment of a waste gas containing fluorine-  
30 containing compounds which comprises the steps of separating the solids from the waste gas, adding H<sub>2</sub> and/or H<sub>2</sub>O or H<sub>2</sub> and/or H<sub>2</sub>O and O<sub>2</sub> as a decomposition assist gas, thermally decomposing the waste gas by contact with  $\gamma$ -alumina at usually at 500 - 1000°C, preferably 600 - 900°C, more  
35 preferably 700 - 900°C, and removing acidic gases from the decomposed waste gas.

In this method, the waste gas containing fluorine-containing compounds may be a waste gas from a semiconductor

fabrication process that contains not only perfluorocarbons and fluorinated hydrocarbons but also oxidizing gases, acidic gases and CO.

The second object of the invention can be attained  
5 by an apparatus for treatment of a waste gas containing  
fluorine-containing compounds which comprises a solids  
treating means for separating the solids from a waste gas  
containing fluorine-containing compounds, an addition means  
for adding H<sub>2</sub> and/or H<sub>2</sub>O or H<sub>2</sub> and/or H<sub>2</sub>O and O<sub>2</sub> as a  
10 decomposition assist gas to the waste gas leaving the solids  
treating means, a thermal decomposing means that is packed  
with  $\gamma$ -alumina heated at 600 - 900°C and which thermally  
decomposes the waste gas to which the decomposition assist  
gas has been added, an acidic gas treating means for  
15 removing acidic gases from the thermally decomposed waste  
gas, and channels for connecting these means in sequence.

In this treatment apparatus, a water scrubber may be  
used as the solids treating means or the acidic gas  
treating means. This treatment apparatus may have not only  
20 an air ejector capable of adjusting the pressure in the  
apparatus through which the waste gas passes but also an  
FT-IR analyzer for controlling the emission density of the  
treated gas.

The first step in the method of the invention for  
25 treating a waste gas containing fluorine-containing  
compounds is passing the waste gas through a solids  
treating means such as a water scrubber. The exit gas is  
passed through a thermal decomposing means packed with  
 $\gamma$ -alumina heated at 500 - 1000°C, preferably 600 - 900°C, and  
30 more preferably 700 - 900°C, with H<sub>2</sub> and/or H<sub>2</sub>O or H<sub>2</sub> and/or  
H<sub>2</sub>O and O<sub>2</sub> being added as a decomposition assist gas, so  
that PFCs, oxidizing gases and CO are completely decomposed  
into acidic gases and CO<sub>2</sub>. The generated acidic gases are  
removed with an acidic gas treating means such as a water  
35 scrubber.

The invention may incorporate not only an air ejector  
capable of adjusting the pressure in the apparatus through  
which the waste gas passes but also an FT-IR analyzer for

controlling the emission density of the treated gas.

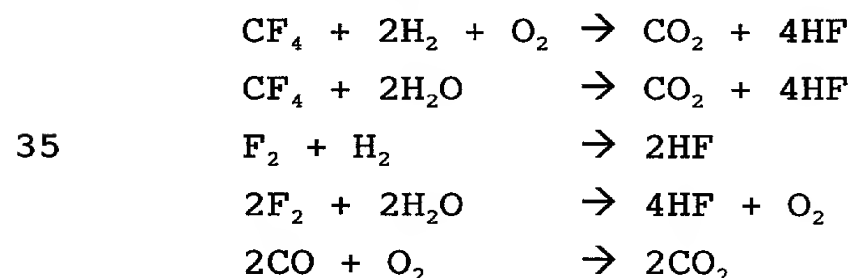
#### BRIEF DESCRIPTION OF THE DRAWING

Fig. 1 is a flowsheet for the waste gas treatment apparatus of the invention.

#### 5 DETAILED DESCRIPTION OF THE INVENTION

The present invention is described below in detail. In the first step, a waste gas containing PFCs, oxidizing gases, acidic gases and CO is passed through a solids treating means such as a water scrubber in order to remove  
10 not only the solids such as  $\text{SiO}_2$  in the waste gas but also Si compounds such as  $\text{SiF}_4$ ,  $\text{SiCl}_4$  and  $\text{SiBr}_4$  that may potentially solidify in the thermal decomposing means at the next stage. If the waste gas is directly introduced into the thermal decomposing means without being passed  
15 through the solids treating means, clogging or other blocking problems will occur, potentially preventing the waste gas from smoothly flowing through the packed  $\gamma$ -alumina layer. The performance of  $\gamma$ -alumina may also deteriorate. By passing the waste gas through the solids  
20 treating means, the solids and the acidic gases containing Si compounds are removed whereas part of oxidizing gases such as  $\text{F}_2$ ,  $\text{Cl}_2$  and  $\text{Br}_2$  as well as all volumes of PFCs and CO are discharged.

The waste gas emerging from the solids treating means  
25 is then introduced into the thermal decomposing means so that it is decomposed through contact with  $\gamma$ -alumina heated at  $500 - 1000^\circ\text{C}$ , preferably  $600 - 900^\circ\text{C}$ , more preferably  $700 - 900^\circ\text{C}$ . On this occasion,  $\text{H}_2$  and/or  $\text{H}_2\text{O}$ ; or  $\text{H}_2$  and/or  $\text{H}_2\text{O}$  and  $\text{O}_2$  are added to the waste gas as a decomposition assist  
30 gas so that the components of the waste gas are decomposed into acidic gases and  $\text{CO}_2$  according to the following reaction schemes:





Thus, PFC reacts with  $H_2$  and  $O_2$  or  $H_2O$  to be decomposed into  $CO_2$  and  $HF$ . Acidic gases such as  $F_2$  react with  $H_2$  or  $H_2O$  to be decomposed to another acidic gas  $HF$ . Carbon monoxide ( $CO$ ) is oxidized to  $CO_2$ .

5 As for PFC,  $H_2$  or  $H_2O$  is added in moles at least equal to the moles necessary for the F atoms in the PFC to be converted to  $HF$  and  $O_2$  is added in moles at least equal to the moles necessary for the C atoms in the PFC to be converted to  $CO_2$ . Preferably,  $O_2$  is added in moles which  
10 are at least equal to the sum of one mole and the above-defined minimum number of moles. As for oxidizing gases,  $H_2$  is introduced in moles at least equal to the moles necessary for the halogen atoms (X) in the oxidizing gas to be converted to an acidic gas (HX).

15 The waste gas leaving the thermal decomposing means only contains the acidic gases (HX) and  $CO_2$  and by subsequent treatment with an acidic gas treating means such as a water scrubber, the acidic gases are completely removed.

20 The alumina to be used in the invention may have a  $\gamma$ -crystalline structure without a uniform pore distribution. While the shape of the alumina is not limited in any particular way, spheres are easy to handle and, hence, preferred. To the extent that will not unduly increase the  
25 resistance to the passage of the waste gas, the particle size of  $\gamma$ -alumina should be as small as possible, preferably between 0.8 mm and 2.6 mm. The  $\gamma$ -alumina may be held at between  $500^\circ C$  and  $1000^\circ C$ , preferably  $600^\circ C$  and  $900^\circ C$  and more preferably  $700^\circ C$  and  $900^\circ C$  during the passage of the waste  
30 gas.

The solids treating means and the acidic gas treating means are preferably a packed column or a spray column on the condition that they are adapted to spray water. The thermal decomposing means should be adapted to permit the  
35 introduction of  $H_2$  and/or  $H_2O$  or  $H_2$  and/or  $H_2O$  and  $O_2$  as a decomposition assist gas.

Fig. 1 is a flowsheet for the waste gas treatment apparatus of the invention. It generally comprises the

solids treating means 1, the  $\gamma$ -alumina packed layer 2, the thermal decomposing means 3, a cleaning water circulating pump 4, the acidic gas treating means 5, an FT-IR analyzer 6, an air ejector 7 and a bypass valve 8.

5        A waste gas 9 containing PFCs, oxidizing gases, acidic gases and CO is first passed through the spray column (solids treating means) 1 so as to remove the solids and Si compounds. The waste gas is then passed through the thermal decomposing means 3 which is also supplied with H<sub>2</sub>,  
10 O<sub>2</sub> and H<sub>2</sub>O to decompose the PFCs, oxidizing gases and CO into acidic gases and CO<sub>2</sub>. The acidic gases are removed by passage through the next spray column (acidic gas treating means) 5, from which the treated gas 10 emerges.

15        The air ejector 7 is installed to control the pressure in each of the treating means and the FT-IR analyzer 6 is provided to monitor the treated gas.

20        Spray water 11 is introduced into the acidic gas treating means 5 and the spent water is forced to the solids treating means 1 with the cleaning water circulating pump 4; the water is used in spraying there and discharged as wastewater 12.

25        The following examples are provided for the purpose of further illustrating the present invention but are in no way to be taken as limiting.

25        Example 1

30        A quartz column of 25 mm $\phi$  was packed with  $\gamma$ -alumina to a height of 100 mm. The  $\gamma$ -alumina was a commercial product of Mizusawa Kagaku K.K. (NEOBEAD GB-08) having a particle size of 0.8 mm. The quartz column was installed in a ceramic electric furnace and the alumina layer was heated at 800°C.

35        In addition to CF<sub>4</sub> diluted with N<sub>2</sub> gas, H<sub>2</sub> and O<sub>2</sub> were supplied as decomposition assist gases, the amount of H<sub>2</sub> being such that the number of H atoms was at least equal to the number of F atoms in CF<sub>4</sub> and the amount of O<sub>2</sub> being at least equimolar to the amount of H<sub>2</sub> introduced. These gases were flowed into the column at a total rate of 408 sccm and their entrance concentrations were 1% (CF<sub>4</sub>), 3.0%

(H<sub>2</sub>) and 5.7% (O<sub>2</sub>).

In order to evaluate the performance of the treatment system, the exit gas was analyzed periodically and the passage of the CF<sub>4</sub> gas was stopped when the removal of CF<sub>4</sub> dropped below 98%. The throughput was determined from the amount of CF<sub>4</sub> that had been passed through the system. The analysis of CF<sub>4</sub> and other gases was conducted with a gas chromatographic apparatus equipped with a mass detector.

As it turned out, the removal of CF<sub>4</sub> dropped to 98% when its passage continued for 920 min. At this point in time, the throughput as determined from the quantity of the supplied CF<sub>4</sub> was 77 L/L. Throughout the experiment, the concentration of CO emission was below the tolerable level (25 ppm).

#### 15 Comparative Example 1

An experiment was conducted using the same equipment as in Example 1 that was packed with the same  $\gamma$ -alumina in the same amount and heated to the same temperature. The total gas flow rate was 408 sccm; the feed gas was a mixture of N<sub>2</sub>-diluted CF<sub>4</sub> and SiF<sub>4</sub>; in addition, H<sub>2</sub> and O<sub>2</sub> were supplied as decomposition assist gases, the amount of H<sub>2</sub> being such that the number of H atoms was at least equal to the total number of F atoms in CF<sub>4</sub> and SiF<sub>4</sub> and the amount of O<sub>2</sub> being at least equimolar to the amount of H<sub>2</sub> introduced. These gases were flowed into the column at respective concentrations of 0.95% (CF<sub>4</sub>), 0.97% (SiF<sub>4</sub>), 5.3% (H<sub>2</sub>) and 6.0% (O<sub>2</sub>).

As it turned out, the removal of CF<sub>4</sub> dropped below 98% when the passage of the CF<sub>4</sub>/SiF<sub>4</sub> gas continued for 510 minutes. At this point in time, the throughput was 40 L/L, which was nearly one half the throughput for the case where only CF<sub>4</sub> gas was supplied. Throughout the experiment, the concentration of CO was below the tolerable level.

#### Example 2

35 An experiment was conducted using the same equipment as in Example 1 that was packed with the same  $\gamma$ -alumina in the same amount and heated to the same temperature. The total gas flow rate was 408 sccm; the feed gas was a

mixture of N<sub>2</sub>-diluted CF<sub>4</sub> and F<sub>2</sub>; in addition, H<sub>2</sub> and O<sub>2</sub> were supplied as decomposition assist gases, the amount of H<sub>2</sub> being such that the number of H atoms was at least equal to the total number of F atoms in CF<sub>4</sub> and F<sub>2</sub> and the amount of O<sub>2</sub> being at least equimolar to the amount of H<sub>2</sub> introduced. These gases were flowed into the column at respective concentrations of 0.92% (CF<sub>4</sub>), 1.1% (F<sub>2</sub>), 5.0% (H<sub>2</sub>) and 6.0% (O<sub>2</sub>).

As it turned out, the removal of CF<sub>4</sub> dropped below 98% when the passage of the CF<sub>4</sub>/F<sub>2</sub> gas continued for 25 hours. At this point in time, the throughput was 115 L/L, which was 1.51 times higher than the throughput for the case where only CF<sub>4</sub> gas was supplied. Throughout the experiment, the concentrations of CO and F<sub>2</sub> were below the tolerable levels (1 ppm for F<sub>2</sub>), provided that F<sub>2</sub> had been decomposed into HF.

#### Reference Example 1

An experiment was conducted using the same equipment as in Example 1 that was packed with the same  $\gamma$ -alumina in the same amount and heated to the same temperature. The total gas flow rate was 408 sccm; in addition to N<sub>2</sub>-diluted CO, O<sub>2</sub> was supplied in moles at least equal to the moles necessary for CO to be converted to CO<sub>2</sub>; their respective entrance concentrations were 1.4% (CO) and 5.7% (O<sub>2</sub>). Throughout the passage of the feed gas for 30 minutes, the concentration of CO was below the detection limit (2 ppm); all of CO had been oxidized to CO<sub>2</sub>.

#### Comparative Example 2

An experiment was conducted using the same equipment as in Example 1 that was packed with the same  $\gamma$ -alumina in the same amount and heated to the same temperature. The total gas flow rate was 408 sccm; in addition to N<sub>2</sub>-diluted CO, H<sub>2</sub>O was supplied at a rate of 0.090 mL/min which was 22 times as much as CO; the entrance concentration of CO was 1.3%.

As it turned out, 1000 ppm of CO leaked as a result of 15-min passage of the feed gas. Obviously, the concentration of CO could not be reduced to below the

tolerable level (25 ppm) by the sole addition of H<sub>2</sub>O.

Reference Example 2

An experiment was conducted using the same equipment as in Example 1 that was packed with the same  $\gamma$ -alumina in the same amount and heated to the same temperature. The total gas flow rate was 408 sccm; in addition to N<sub>2</sub>-diluted CO, H<sub>2</sub>O was supplied at a rate of 0.090 mL/min which was 18 times as much as CO and O<sub>2</sub> was supplied in moles at least equal to the moles necessary for CO to be converted to CO<sub>2</sub>; the entrance concentrations of CO and O<sub>2</sub> were 1.5% and 3.4%, respectively.

As it turned out, the concentration of CO had been reduced to below the detection limit (2 ppm) after the passage of the feed gas for 3 hours. Obviously, CO was oxidized to CO<sub>2</sub> by addition of O<sub>2</sub>.

Example 3

An experiment was conducted using the same equipment as in Example 1 that was packed with the same  $\gamma$ -alumina in the same amount and heated to 700°C. The total gas flow rate was 408 sccm; in addition to N<sub>2</sub>-diluted CF<sub>4</sub>, H<sub>2</sub>O was supplied at a rate of 0.040 mL/min which was 14 times as much as CF<sub>4</sub> and O<sub>2</sub> was supplied in moles at least equal to the moles necessary for the C atom in CF<sub>4</sub> to be converted to CO<sub>2</sub>; the entrance concentrations of CF<sub>4</sub> and O<sub>2</sub> were 0.89% and 3.0%, respectively.

As it turned out, the removal of CF<sub>4</sub> dropped below 98% when the passage of the feed gas continued for 23 hours. At this point in time, the throughput was 110 L/L, which was 1.4 times higher than the throughput of CF<sub>4</sub> treatment in the presence of added H<sub>2</sub> and O<sub>2</sub>. Throughout the experiment, the concentration of CO was below the tolerable level.

Comparative Example 3

In order to evaluate the effectiveness of the wet process in treating oxidizing gases and acidic gases, a water cleaning column (210 mm<sup>φ</sup> x 430 mm<sup>H</sup> with a Raschig ring packed to a height of 170 mm) was supplied with a waste gas at a total rate of 60 L/min and spray water at a

rate of 3.5 L/min. The waste gas was prepared from  $F_2$ ,  $SiF_4$  and  $Cl_2$  which had entrance concentrations of 1100 ppm, 1600 ppm and 5100 ppm, respectively. At the exit of the column,  $F_2$ ,  $SiF_4$  and  $Cl_2$  were detected at concentrations of 11 ppm, < 1 ppm, and 3300 ppm, respectively. Obviously,  $SiF_4$  was effectively treated but  $F_2$  and  $Cl_2$  leaked out.

#### Example 4

A water cleaning column (210 mm<sup>φ</sup> x 430 mm<sup>H</sup> with a Raschig ring packed to a height of 170 mm) was used as a solids treating means. This column was combined with a thermal decomposing means comprising a preheating chamber and a catalyst packed chamber and an acidic gas treating means which was the same as the water cleaning column. The exit gas leaving the acidic gas treating means was monitored with an FT-IR analyzer (Infinity 6000 of MATTSON) and the pressure in the experimental system was controlled with an air ejector of Daito Seisakusho K.K. The solids treating means and the acidic gas treating means were supplied with cleaning water at respective flow rates of 2 L/min and 4 L/min. The thermal decomposing means was supplied with air and pure water at respective flow rates of 10 L/min and 2.4 mL/min. The catalyst was 15 L of  $\gamma$ -alumina (NEOBEAD GB-08 of Mizusawa Kagaku K.K.)

A gas dryer (MD-70-72P of PERMAPUR) was installed ahead of the FT-IR analyzer for removing the moisture in the waste gas. Air was supplied into the air ejector at a rate of 30 L/min so that the pressure in the system was kept at a negative value of -0.5 kPa. A waste gas was introduced at a flow rate of 60 L/min and it was prepared from a  $N_2$  base containing  $CF_4$ ,  $SiF_4$ ,  $F_2$  and CO at respective concentrations of 0.5%, 0.3%, 0.3% and 0.3%. The waste gas was first passed through the solids treating means, then passed through the thermal decomposing means in the presence of added water and  $O_2$ , with the catalyst bed being heated at 700°C. The waste gas was subsequently passed through the acidic gas treating means and the treated gas was continuously analyzed by FT-IR. After the passage of the waste gas for 10 hours,  $CO_2$  was detected in an amount

of 6900 ppm but each of  $\text{CF}_4$ ,  $\text{SiF}_4$ , HF and CO had been treated to below 1 ppm. No  $\text{F}_2$  was detected by ion chromatographic analysis.

Example 5

5        A waste gas treatment was conducted with the same experimental setup under the same conditions as in Example 4, except that  $\text{CF}_4$  was replaced by  $\text{C}_2\text{F}_6$  and that the waste gas was prepared from a  $\text{N}_2$  base containing  $\text{C}_2\text{F}_6$ ,  $\text{SiF}_4$ ,  $\text{F}_2$  and CO at respective concentrations of 0.5%, 0.3%, 0.3% and  
10    0.3%. The waste gas was passed through the solids treating means, the thermal decomposing means and the acidic gas treating means.

      The treated gas emerging from the acidic gas treating means was continuously analyzed by FT-IR. After the  
15    passage of the waste gas for 10 hours,  $\text{CO}_2$  was detected in an amount of 11000 ppm but each of  $\text{C}_2\text{F}_6$ ,  $\text{SiF}_4$ , HF and CO had been treated to below 1 ppm. No  $\text{F}_2$  was detected by ion chromatographic analysis.

      According to the invention, harmful waste gases from  
20    the semiconductor fabrication process that contain PFCs, oxidizing gases, acidic gases and CO and which are a potential accelerator of global warming can be treated in such a way that high percent decomposition is maintained for a prolonged time.

WHAT IS CLAIMED IS:

1. A method for treatment of a waste gas containing fluorine-containing compounds which comprises the steps of separating the solids from the waste gas, adding  $H_2$  and/or  $H_2O$  or  $H_2$  and/or  $H_2O$  and  $O_2$  as a decomposition assist gas, thermally decomposing the waste gas by contact with  $\gamma$ -alumina at  $500 - 1000^\circ C$ , and removing acidic gases from the decomposed waste gas.
2. The method according to claim 1, wherein the temperature used in the thermally decomposing step ranges from  $600 - 900^\circ C$
3. The method according to claim 1, wherein said waste gas containing fluorine-containing compounds contains perfluoro-carbons and fluorinated hydrocarbons as well as oxidizing gases, acidic gases and CO.
4. The method according to claim 3, wherein said waste gas containing fluorine-containing compounds is a waste gas from a semiconductor fabrication process.
5. An apparatus for treatment of a waste gas containing fluorine-containing compounds which comprises a solids treating means for separating the solids from a waste gas containing fluorine-containing compounds, an addition means for adding  $H_2$  and/or  $H_2O$ ; or  $H_2$  and/or  $H_2O$  and  $O_2$  as a decomposition assist gas to the waste gas leaving the solids treating means, a thermal decomposing means that is packed with  $\gamma$ -alumina heated at  $500 - 1000^\circ C$  and which thermally decomposes the waste gas to which the decomposition assist gas has been added, an acidic gas treating means for removing acidic gases from the thermally decomposed waste gas, and channels for connecting these means in sequence.
6. The apparatus according to claim 5, wherein said solids treating means or said acidic gas treating means is a water scrubber.
7. The apparatus according to claim 5 or 6, which has not only an air ejector capable of adjusting the pressure in the apparatus through which the waste gas passes but also an FT-IR analyzer for controlling the emission density of the treated gas.

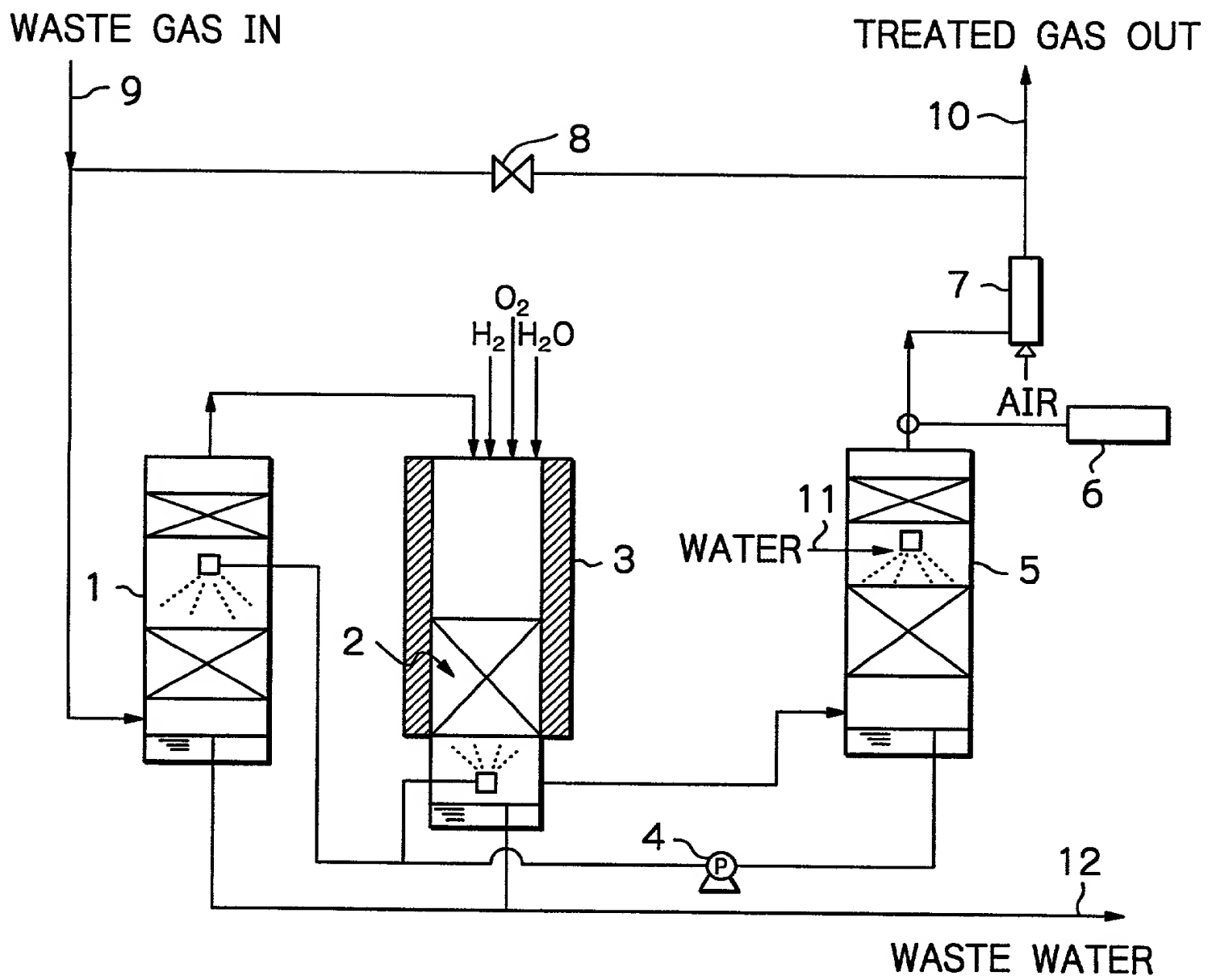


METHOD AND APPARATUS FOR TREATING A WASTE GAS  
CONTAINING FLUORINE-CONTAINING COMPOUNDS

ABSTRACT OF THE DISCLOSURE

The improved apparatus for treatment of a waste gas  
5 containing fluorine-containing compounds comprises solids  
treating means 1 for separating the solids from a waste gas  
containing fluorine-containing compounds, addition means  
for adding  $H_2$  and/or  $H_2O$  or  $H_2$  and/or  $H_2O$  and  $O_2$  as a  
decomposition assist gas to the waste gas leaving the solids  
10 treating means, thermal decomposing means 3 that is packed  
with  $\gamma$ -alumina 2 heated at  $600 - 900^\circ C$  and which thermally  
decomposes the waste gas to which the decomposition assist  
gas has been added, acidic gas treating means 5 for removing  
acidic gases from the thermally decomposed waste gas, and  
15 channels for connecting these means in sequence. The  
apparatus preferably includes air ejector 7 capable of  
adjusting its internal pressure.

Fig. 1



**DECLARATION AND POWER OF ATTORNEY FOR U.S. PATENT APPLICATION**

☒ Original      ☐ Supplemental      ☐ Substitute      ☐ PCT      ☐ Design

As a below named inventor, I hereby declare that: my residence, post office address and citizenship are as stated below next to my name; that I verily believe that I am the original, first and sole inventor (if only one name is listed below) or an original, first and joint inventor (if plural inventors are named below) of the subject matter which is claimed and for which a patent is sought on the invention entitled:

Title: METHOD AND APPARATUS FOR TREATING A WASTE GAS CONTAINING  
FLUORINE-CONTAINING COMPOUNDS

of which is described and claimed in:

☒ the attached specification, or

☐ the specification in the application Serial No. \_\_\_\_\_ filed \_\_\_\_\_;  
and with amendments through \_\_\_\_\_ (if applicable), or

☐ the specification in International Application No. PCT/ \_\_\_\_\_, filed \_\_\_\_\_, and as amended  
on \_\_\_\_\_ (if applicable).

I hereby state that I have reviewed and understand the content of the above-identified specification, including the claims, as amended by any amendment(s) referred to above.

I acknowledge my duty to disclose to the Patent and Trademark Office all information known to me to be material to patentability as defined in Title 37, Code of Federal Regulations, §1.56.

I hereby claim priority benefits under Title 35, United States Code, §119 (and §172 if this application is for a Design) of any application(s) for patent or inventor's certificate listed below and have also identified below any application for patent or inventor's certificate having a filing date before that of the application on which priority is claimed:

COUNTRY	APPLICATION NO.	DATE OF FILING	PRIORITY CLAIMED
Japan	328411/1999	November 18, 1999	Yes

I hereby claim the benefit under Title 35, United States Code, §120 of any United States application(s) listed below and, insofar as the subject matter of each of the claims of this application is not disclosed in the prior United States application in the manner provided by the first paragraph of Title 35, United States Code, §112, I acknowledge the duty to disclose information material to patentability as defined in Title 37, Code of Federal Regulations, §1.56 which occurred between the filing date of the prior application and the national or PCT international filing date of this application.

APPLICATION SERIAL NO.	U.S. FILING DATE	STATUS: PATENTED, PENDING, ABANDONED

And I hereby appoint John T. Miller, Reg. No. 21,120; Michael R. Davis, Reg. No. 25,134; Matthew M. Jacob, Reg. No. 25,154; Jeffrey Nolton, Reg. No. 25,408; Warren M. Cheek, Jr., Reg. No. 33,367; Nils E. Pedersen, Reg. No. 33,145 and Charles R. Watts, Reg. No. 33,142, who together constitute the firm of WENDEROTH, LIND & PONACK, L.L.P., attorneys to prosecute this application and to transact all business in the U.S. Patent and Trademark Office connected therewith.

I hereby authorize the U.S. attorneys named herein to accept and follow instructions from YUASA AND HARA as to any action to be taken in the U.S. Patent and Trademark Office regarding this application without direct communication between the U.S. attorneys and myself. In the event of a change in the persons from whom instructions may be taken, the U.S. attorneys named herein will be so notified by me.

Send Correspondence to

WENDEROTH, LIND & PONACK, L.L.P.  
2033 K Street, N.W., Suite 800  
Washington, DC 20006

Direct Telephone Calls to:

WENDEROTH, LIND & PONACK, L.L.P.  
Area Code (202) 721-8200

Direct Facsimile Messages to:

Area Code (202) 721-8250

Full Name of First Inventor	FAMILY NAME MORI	FIRST GIVEN NAME Yoichi	SECOND GIVEN NAME
Residence & Citizenship	CITY Kanagawa-ken	STATE OR COUNTRY Japan	COUNTRY OF CITIZENSHIP Japan
Post Office Address	ADDRESS 1-6-18, Jukkenzaka, Chigasaki-shi,	CITY Kanagawa-ken,	STATE OR COUNTRY Japan
Full Name of Second Inventor	FAMILY NAME KYOTANI	FIRST GIVEN NAME Takashi	SECOND GIVEN NAME
Residence & Citizenship	CITY Kanagawa-ken	STATE OR COUNTRY Japan	COUNTRY OF CITIZENSHIP Japan
Post Office Address	ADDRESS 85-1-101, Sachigaoka, Yokohama-shi,	CITY Kanagawa-ken,	STATE OR COUNTRY Japan
Full Name of Third Inventor	FAMILY NAME SHINOHARA	FIRST GIVEN NAME Toyoji	SECOND GIVEN NAME
Residence & Citizenship	CITY Tokyo	STATE OR COUNTRY Japan	COUNTRY OF CITIZENSHIP Japan
Post Office Address	ADDRESS 1-27-4, Kitamachi, Nerima-ku,	CITY Tokyo,	STATE OR COUNTRY Japan
Full Name of Fourth Inventor	FAMILY NAME	FIRST GIVEN NAME	SECOND GIVEN NAME
Residence & Citizenship	CITY	STATE OR COUNTRY	COUNTRY OF CITIZENSHIP
Post Office Address	ADDRESS	CITY	STATE OR COUNTRY ZIP CODE

<b>Full Name of Fifth Inventor</b>	<b>FAMILY NAME</b>	<b>FIRST GIVEN NAME</b>	<b>SECOND GIVEN NAME</b>
<b>Residence &amp; Citizenship</b>	<b>CITY</b>	<b>STATE OR COUNTRY</b>	<b>COUNTRY OF CITIZENSHIP</b>
<b>Post Office Address</b>	<b>ADDRESS</b>	<b>CITY</b>	<b>STATE OR COUNTRY</b> <b>ZIP CODE</b>

<b>Full Name of Sixth Inventor</b>	<b>FAMILY NAME</b>	<b>FIRST GIVEN NAME</b>	<b>SECOND GIVEN NAME</b>
<b>Residence &amp; Citizenship</b>	<b>CITY</b>	<b>STATE OR COUNTRY</b>	<b>COUNTRY OF CITIZENSHIP</b>
<b>Post Office Address</b>	<b>ADDRESS</b>	<b>CITY</b>	<b>STATE OR COUNTRY</b> <b>ZIP CODE</b>

<b>Full Name of Seventh Inventor</b>	<b>FAMILY NAME</b>	<b>FIRST GIVEN NAME</b>	<b>SECOND GIVEN NAME</b>
<b>Residence &amp; Citizenship</b>	<b>CITY</b>	<b>STATE OR COUNTRY</b>	<b>COUNTRY OF CITIZENSHIP</b>
<b>Post Office Address</b>	<b>ADDRESS</b>	<b>CITY</b>	<b>STATE OR COUNTRY</b> <b>ZIP CODE</b>

I further declare that all statements made herein of my own knowledge are true, and that all statements on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code, and that such willful false statements may jeopardize the validity of the application or any patent issuing thereon.

1st Inventor Yoichi Mori (Yoichi MORI) Date November 7, 2000  
 2nd Inventor Takashi Kyotani (Takashi KYOTANI) Date November 7, 2000  
 3rd Inventor Toyoji Shinochara (Toyoji SHINOHARA) Date November 7, 2000  
 4th Inventor \_\_\_\_\_ Date \_\_\_\_\_  
 5th Inventor \_\_\_\_\_ Date \_\_\_\_\_  
 6th Inventor \_\_\_\_\_ Date \_\_\_\_\_  
 7th Inventor \_\_\_\_\_ Date \_\_\_\_\_

The above application may be more particularly identified as follows:

U.S. Application Serial No. \_\_\_\_\_ Filing Date \_\_\_\_\_  
 Applicant Reference Number \_\_\_\_\_ Atty Docket No. \_\_\_\_\_  
 Title of Invention \_\_\_\_\_  
 \_\_\_\_\_